WOOD-LIQUID RELATIONS

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INTRODUCTION

Substantially every important property of wood is affected by the presence of some liquid, in one form or another, that is normally in contact with and usually distributed through the wood under the conditions of its commercial use. It seems unnecessary, therefore, to debate the practical importance of fundamental studies of the relations between wood and liquids or to catalogue the instances where information gained from such studies has been of direct practical service. In justification of investigative work of this kind, it should be sufficient merely to point out that the many important practical problems in connection with the drying and the impregnation of wood, the shrinkage of wood, and the numerous uses of wood in which liquids affect the properties seriously, all have their origins in the fundamental relations between wood and liquids.

A large amount of general information on this subject has been obtained from observation of the practical problems involved both

in using wood and in preparing it for use, and from extensive experimentation in these problems. There is also available a considerable quantity of fragmentary data on the more fundamental aspects of wood-liquid relations. Besides these sources of information there are many studies of phenomena of the same kind occurring between liquids and substances other than wood, and also much information on the minute structure of the material, a subject prerequisite to any adequate treatment of wood-liquid relations.
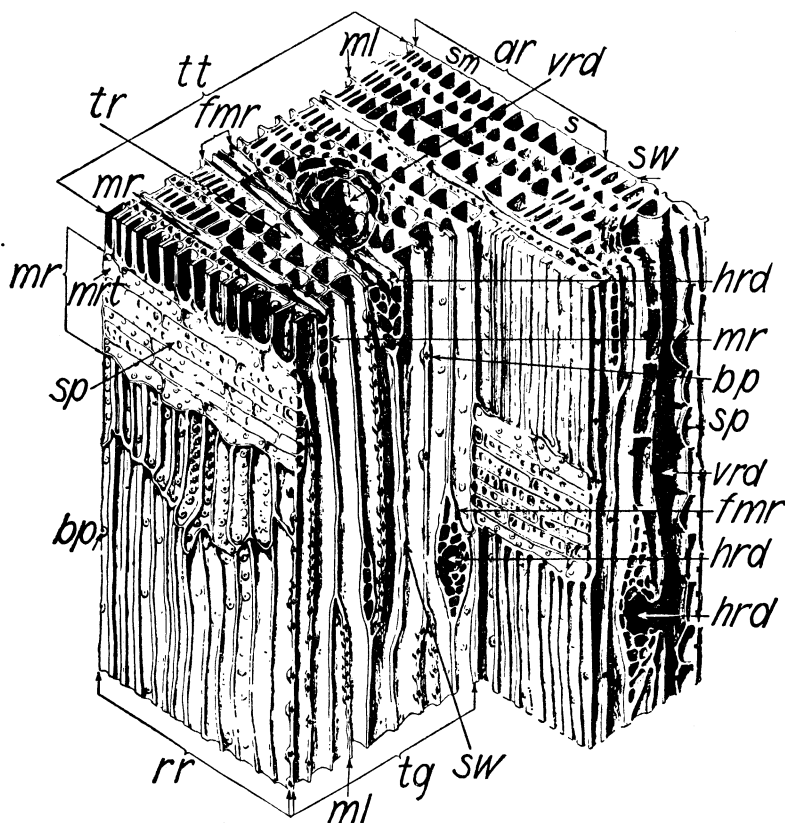
FIGURE 1.—A magnified block of a typical softwood: *ar*, Annual growth ring; *bp*, bordered pit; *fmr*, fusiform wood ray; *hrd*, horizontal resin canal or duct; *ml*, middle lamella; *mr*, wood ray; *mrt*, wood ray tracheid; *rr*, radial surface; *s*, spring wood; *sm*, summer wood; *sp*, simple pit; *sw*, secondary wall; *tg*, tangential surface; *tr*, tracheid; *tt*, transverse surface; *vrd*, vertical resin canal or duct

The primary purpose of this bulletin is to summarize the present knowledge of wood-liquid relations and to prepare the way for a series of publications reporting experimental research on various parts of the general problem. The most significant portions of the available information about wood-liquid relations and wood structure will be included in this presentation of the subject and will be correlated as far as possible by means of the general physical laws applicable.

THE STRUCTURE OF WOOD

SOFTWOODS

Perhaps the best way to show the general structure of wood is by means of enlarged and somewhat idealized drawings of specimen blocks of wood, as shown in Figures 1 and 2. Figure 1 represents a
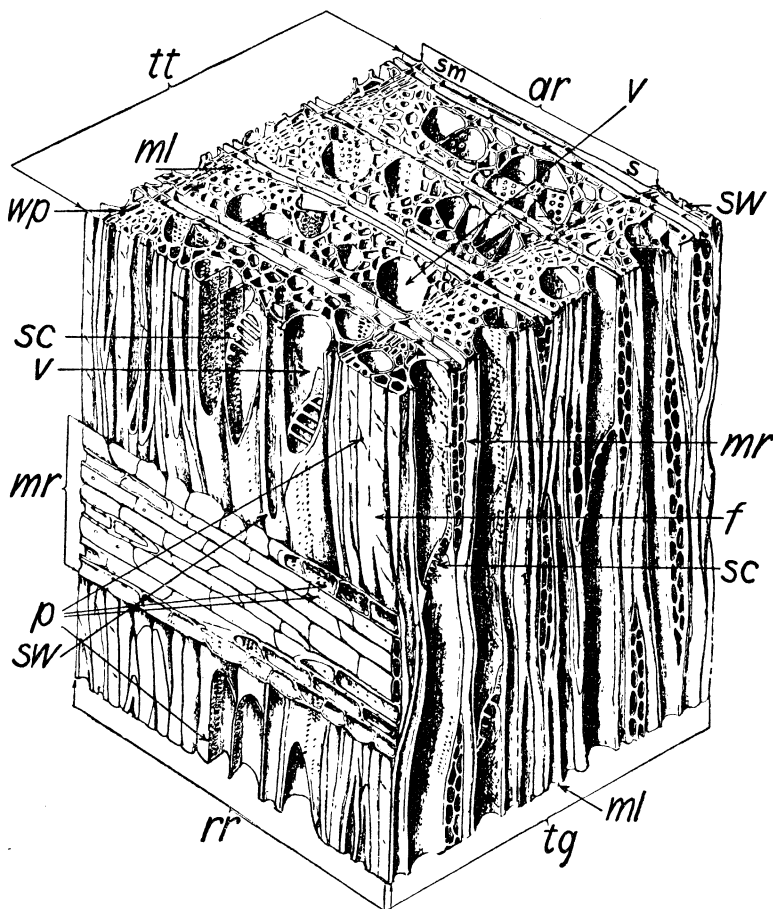
FIGURE 2.—A magnified block of a typical hardwood: *ar*, Annual growth ring; *f*, fiber; *ml*, middle lamella; *mr*. wood ray; *p*, pit; *rr*, radial surface; *s*, spring wood; *sc*, scalariform perforation between vessels; *sm*, summer wood; *sw*, secondary wall; *tg*, tangential surface; *tt*, transverse surface; *v*, vessel or pore; *wp*, wood parenchyma

block of wood, one-fourth of an inch on the longer edges, of northern white pine [3] (*Pinus strobus*), which may be considered typical of the softwoods (gymnosperms). The vertical direction in the block represents the vertical direction in the tree from which the block was cut. Since most of the structural elements of the wood

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[3] The names of species of wood appearing in this bulletin, other than unverifiable quoted ones, are the standard common names given in the Check List of the Forest Trees of the United States (*25*).

lie in this direction, it is commonly called longitudinal. The direction represented by the line *ar*, from the bark of the tree to the pith, is called the radial direction. The third direction, represented by the line *tg*, at right angles to the other two, is called tangential.

The main part of the block in Figure 1 is made up of the walls of a series of longitudinal (vertical) cells, *tr*. These are called fibers or, in stricter terminology, tracheids. The end of one series of tracheids and the beginning of another is shown halfway up the left side surface, *rr*. Contiguous tracheids possess in common a median wall layer, the middle lamella, *ml*, which appears to be a cementing layer. The other tubular longitudinal spaces, larger than the cavities in the tracheids, are the vertical resin canals (sometimes called resin ducts), *vrd*. These are surrounded by specialized cells, shorter than the tracheids, which are capable of secreting resin.

The radial structures *mr* are called wood rays. The cells composing them, which are much shorter than the tracheids, are called ray cells. Some of the radial bands of ray cells contain a horizontal resin canal, *hrd*, which communicates directly with a vertical canal, as shown near the lower right corner of the block. There are no main structural elements leading in a tangential direction, but there are means of communication between the tracheids in the tangential direction, the bordered pits, *bp*. Further communication by means of simple pits (*sp*) exists between the tracheids and the wood rays. Bordered pits are thin, circular spots in the cell wall, called pit membranes, over which the unthinned wall extends in a domelike formation that is open at the top. In a simple pit, on the other hand, the unthinned wall does not project over the thinned portion. A pit may be bordered on one side and simple on the other.

Some tracheids are larger in cross section and have relatively thinner walls than others. The large tracheids, which are formed in the earlier part of the season's growth, make up the spring wood, *s*. The later growth of thicker walled tracheids forms the summer wood, *sm*. The spring wood and summer wood together form the annual growth ring, *ar*. The growth bands can usually be seen with the naked eye in the cross section of a piece of wood.

The other softwoods have a general structure very similar to that of northern white pine. Some have larger and some smaller resin canals, and in others these canals are wholly lacking. Aside from this, however, there are no major differences.

HARDWOODS

The hardwoods (angiosperms) as a class, on the other hand, have some major features distinguishing them from the softwoods. These are shown in Figure 2, which represents a cube of yellow poplar (*Liriodendron tulipifera*) of the same over-all size as the block in Figure 1. In addition to the fibers like *f*, which have a purely mechanical function, the hardwoods possess characteristic longitudinal structures of prominence, the vessels or ducts *v*, which in a cross section are called pores. Vessels are composite structures made up of segments or large cells arranged in rows that are vertical in the tree trunk. The vessel segments are shorter and much larger in diameter than the fibers around them, and besides their cavities are joined end to end, instead of side to side, through relatively

large openings, *sc.* The hardwood fibers are generally shorter and smaller in diameter than the softwood tracheids. The pits *p* in the fibers of the hardwoods are much smaller and less numerous and hence less conspicuous than those in the tracheids of the soft-woods.

Although the hardwoods may or may not have larger and more thinly walled fibrous tissue in the spring wood than in the summer wood, in many species the spring wood is characterized by the presence of pores much larger than those found in the summer wood. Such hardwoods are known as ring-porous woods. In others, the diffuse-porous woods, the pores are more nearly the same size and are fairly evenly distributed through the annual growth ring. The middle lamella, *ml*, the annual growth rings, *ar*, and the wood rays, *mr*, of the hardwoods are similar to those of the softwoods, although the wood rays are larger.

DIMENSIONS OF WOOD ELEMENTS

The average length of the tracheids in softwoods may vary from 1.5 to 8 mm., and the inside diameter from 0.005 to 0.05 mm. The ends of longitudinally adjacent tracheids overlap from one-tenth to one-fourth of their length, and the bordered pits usually are most abundant in the overlapping portions. In the hardwoods the fibers average about 1 mm. in length, and the range in the diameter of the cell lumina is from about 0.003 mm. for the smaller fibers to approximately 0.4 mm. for the larger vessels. In addition to these details of structure, which are visible under the microscope, it has recently been shown *(21)*[4] that there are openings extending from tracheid to tracheid, which are probably through the membranes of the pits, of unknown shape but with effective diameters (the diameters of true circles having the same effect) as follows:

Range in maximum diameters of five species: $68m\mu$ to $184m\mu$.[5]
Range in average diameters of two species: $11m\mu$ to $23m\mu$.
These diameters apply definitely to softwoods only, although it is likely that the pit pores of hardwoods also fall within the same limits.

STATICS

The static relationships of wood-liquid systems are of primary importance, since they control the equilibrium conditions that in turn govern the absorption of liquids by wood and thus not only determine the amount of variation in the physical properties affected by the presence of liquids but also influence the dynamic relationships. In fact many of the dynamic changes are due directly to lack of equilibrium in the static relationships.

Accurate details concerning the static relations between wood and liquids are largely wanting. This situation comes partly from lack of proper investigations and partly from difficulties in distinguishing between the effects caused solely by the wood substance and the modifications of these effects by the complex wood structure. In all of the following discussion of statics, it will be necessary to consider first the theoretical relations between the liquids and the

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[4] Italic numbers in parentheses refer to Literature Cited, p. 32.
[5] The Greek letter mu (μ) represents one-millionth part of a meter; a millimicron (mμ) is one-thousandth of a micron.

wood substance and then the possible effects of structure. For simplicity it will also be necessary to consider the equilibriums of wood substance as a whole, without any attempt to distinguish between different parts.

ABSORPTION IN GENERAL

The static relations between wood and liquids considered here belong to the general class of phenomena grouped under the term " absorption." Various other terms, such as " adsorption," " sorption," " imbibition," and " solid solution," have been used to differentiate various types of absorption from the standpoint either of the gross effects or of the mechanism by which the effects are obtained. This study is not concerned with such differentiation; the matter is largely controversial, and there is nothing to be gained by including a discussion of it in this attempt to correlate the absorption effects of wood. On the other hand, the general laws governing the similar absorption effects of other materials will be of value. This bulletin will therefore use the general term " absorption " in referring to the static relations between wood and liquids.

ABSORPTION OF WATER

From the commercial standpoint the absorption of water by wood substance is more important than that of other liquids. Further, the absorption effects of water are greater, and there is more information available on such absorption. This bulletin will therefore take up water absorption first and will then describe the effects of other liquids through comparison with those of water. The absorption of water by wood belongs to the general class of absorptions of liquids by elastic jellies and is almost exactly analogous to the absorptions of water by various cellulosic fibrous materials. These absorptions are characterized by heat of absorption, swelling of the fibrous material, decrease in the vapor pressure of the water absorbed, various changes in physical properties of the fibers, and a comparatively low limit for the water absorbed.

HEAT OF ABSORPTION

The heat given off during the absorption of water by wood is a measure of the strength of the combination and bears a quantitative relationship to the other measures of energy change. Dunlap [6] has determined the total heat of absorption of water by wood at 0° C., finding that for several species there is a range from 14.6 to 19.6 calories per gram of wood. Rosenbohm (15) obtained 20.8 calories per gram for the heat of wetting of cotton cellulose by water. Volbehr (31) has also determined the heat of absorption of different amounts of water by wood, from 2 per cent up to complete saturation, as shown in Figure 3. Katz (4) has shown that cotton cellulose gives a very similar curve.

SWELLING OF WOOD

The amount of swelling of wood substance that accompanies the absorption of water has never been determined with any degree of

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[6] DUNLAP, F.   HEAT OF ABSORPTION OF WATER IN WOOD.   Unpublished report.   1913.

completeness or accuracy. The only direct known information on the subject consists of a few measurements by Roth (*16*), who found that the cell wall in microsections of longleaf pine and of northern white pine decreased in thickness during drying 15 to 31 per cent of the thickness when wet. It is probable that such wide variation is due to lack of control of the dryness during the measurements, since the publication does not mention this control. The only indirect quantitative information available is that obtained from the specific gravities of wood substance and water, together with the amount of water absorbed during swelling. The specific gravity of wood substance is about 1.52, and if during swelling the wood substance absorbs (as will be seen later in this bulletin) about 29 per
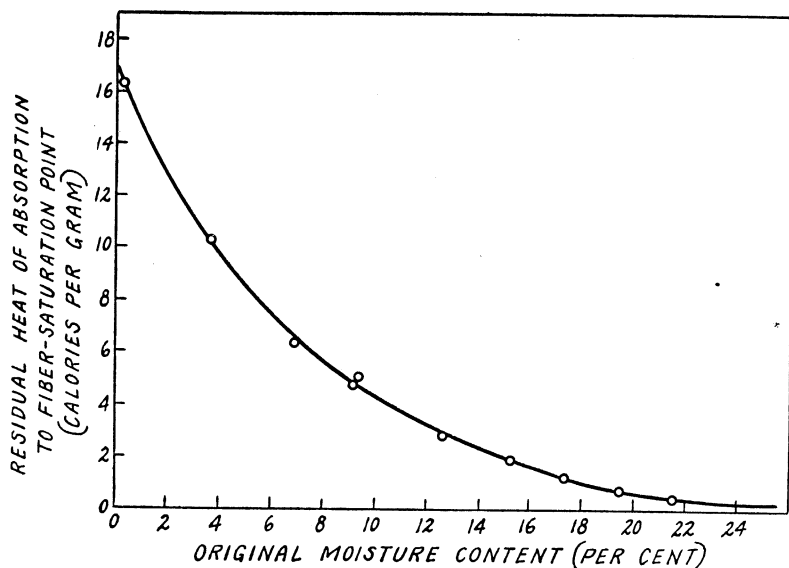
FIGURE 3.—The relation between change in original moisture content and residual heat of absorption for pine-wood flour as the moisture content increases to the fiber-saturation point

cent by weight of water having a specific gravity of 1 the volume of the swollen wood should be 144.1 per cent that of the original dry wood:

$$\frac{\dfrac{1}{1.52}+\dfrac{0.29}{1.00}}{\dfrac{1}{1.52}}=1.441$$

This computation involves the assumptions that there is no compression of the water during the absorption and that there are no pre-existing cavities occupied by the absorbed water (*22*), which assumptions are only approximately correct. A swelling of 44.1 per cent of the dry volume is the same as a shrinkage of 30.6 per cent of the green volume, and this value thus corresponds to the upper figures given by Roth.

FIGURE 4.—The moisture-content values of Sitka spruce at equilibrium with various temperatures, partial vapor pressures, and relative humidities

Although a large amount of data on the swelling and shrinking of blocks and boards has been published, such information is not suitable for fundamental consideration on account of the effect of the wood structure on the transmission 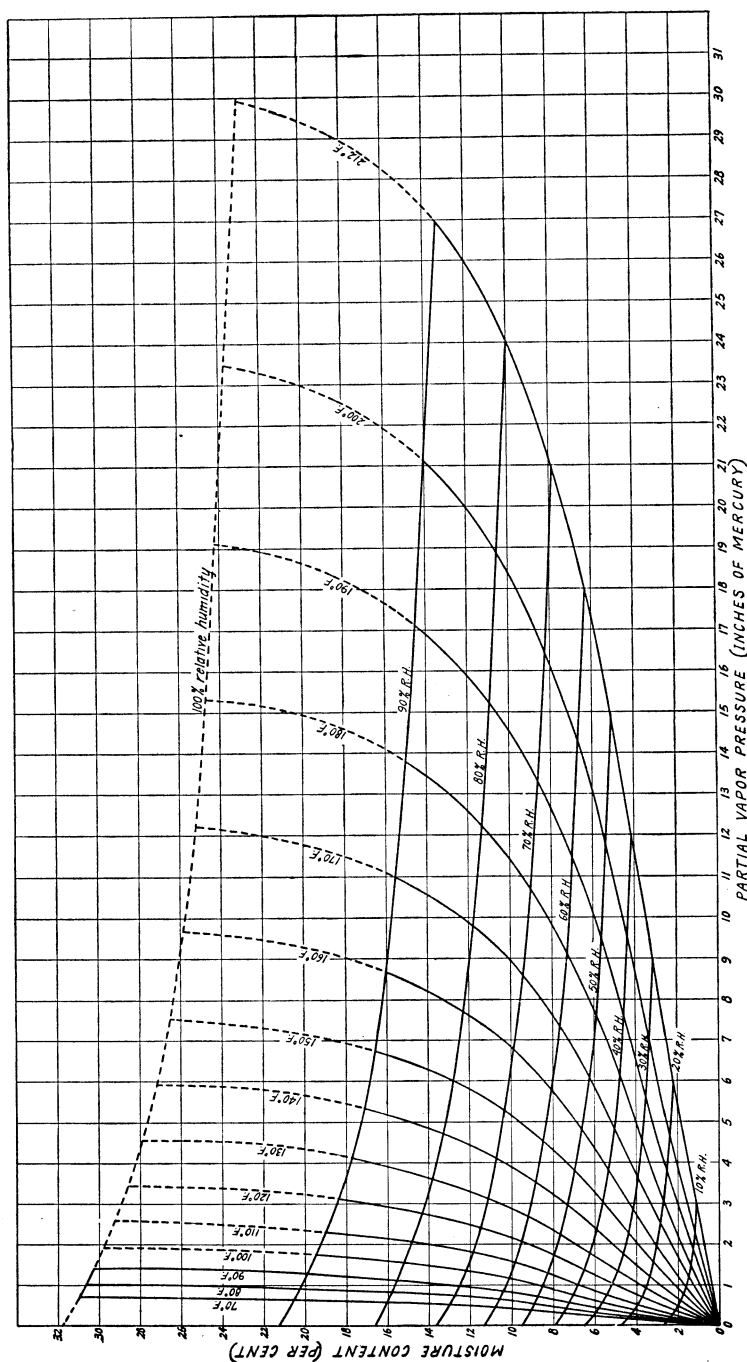of the swelling of the wood substance to the external dimensions of the block. Roth has shown one instance in which only one-third of the shrinkage of the cell wall was effective in changing the outside dimensions of a microsection. There is a wide variation in the shrinkage of the outside dimensions of blocks, not only in different species but also in different directions in the wood. And, further, difference in the conditions of drying, which affect the degree of surface set in casehardened pieces, likewise causes variation in such shrinkage. For instance, in measurements made on a large number of species grown in the United States (*10, 12*) the volumetric shrinkage from a saturated to an oven-dry condition varied from 7.3 to 25 per cent, the linear tangential shrinkage from 3.6 to 15.3 per cent, and the radial from 2.1 to 8.2 per cent. The longitudinal shrinkage of normal wood is only a few tenths of 1 per cent (*5*). It is probable that these variations in outside shrinkage are due entirely to variation in the wood structure and not to any variation in the amount of shrinkage of the wood substance.

Differential swelling measurements (*3, 29, 13*) have been made only on pieces of considerable size so that they do not give accurate quantitative relationships between absorbed water and swelling, although they do show the general relationship. This relationship appears to be linear over the whole range of water absorption except, perhaps, in the immediate vicinity of the fiber-saturation point, where the data are less reliable anyway.

EFFECT OF ABSORPTION ON VAPOR PRESSURE

The effect of absorption on the vapor pressure of the water absorbed is shown in the curves of Figure 4. The shape of these curves corresponds to that of Figure 3 in that the greater diminution of vapor pressure is accompanied by the greater heat of absorption. The data expressed in these two sets of curves were obtained from two species of wood only, pine and Sitka spruce, and other species might show some slight variations. The general shape of the curves, however, would be the same for all species.

The solid lines in the curves [7] of Figure 4 are based on experimental data; the dotted parts of the lines are calculated.

EFFECT OF MOISTURE CONTENT ON STRENGTH

The effect of absorbed moisture on the strength of wood has been determined for a considerable number of species. The general form of the curves for all the species tested is shown in Figure 5, which records the results of different strength tests of Sitka spruce. The point at which there is no further change in strength with change in moisture content seems to vary somewhat with the species and perhaps with the type of test. At present there is no explanation for this apparent variation.

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[7] The data represented in these curves are the work of W. K. Loughborough.

EFFECT OF MOISTURE CONTENT ON ELECTRICAL PROPERTIES

Stamm (*20, 23*) has recently studied the quantitative relationship between the moisture content and the electrical conductivity of wood
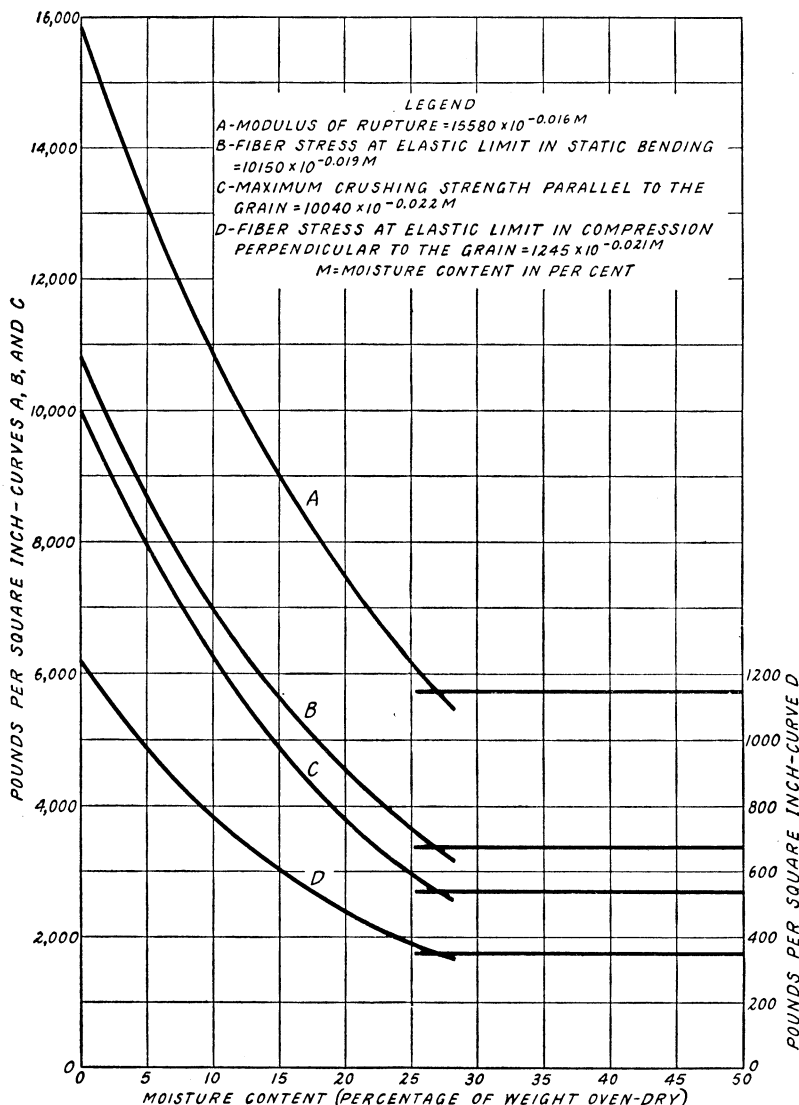

FIGURE 5.—The relation between the strength and the moisture content of small, clear specimens of Sitka spruce

substance. He found that the logarithm of the conductivity varied directly as the percentage of absorbed water, up to the fiber-saturation point; Figure 6 gives a typical curve showing this relationship. As with previously mentioned properties, the absorbed water

has a quantitative effect different from that of the free water; the curve indicates this fact. Table 1 shows that electrical resistance, like many other properties, is different in the different directions in wood.
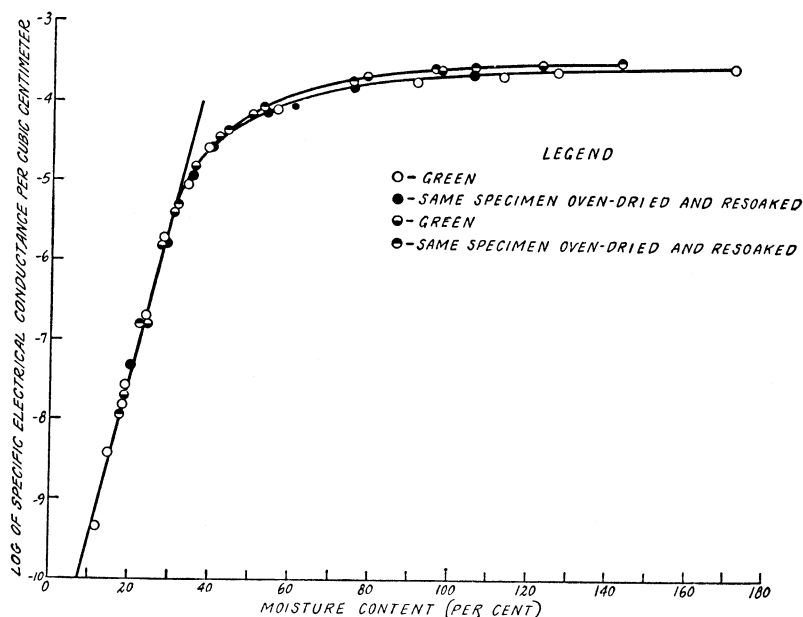
FIGURE 6.—The effect of moisture content on the specific electrical conductance of nonextracted redwood

TABLE 1.—*Typical variation in the electrical resistance of wood in its different structural directions*

Species	Mois- ture con- tent	Electrical resistance		
		Longi- tudinal	Radial	Tangen- tial
	Per cent	*Megohms*	*Megohms*	*Megohms*
Western red cedar	14.0	9	22	24
Sitka spruce	15.7	10	18	20
Alaska cedar	15.6	18	27	27
Douglas fir	15.3	11	21	23

The condensive capacity of wood under different moisture-content values would not be expected to show a change in value at the fiber-saturation point but should remain directly proportional to the relative amounts of wood and of water and to their dielectric constants (specific inductive capacities). There are no experimental data available to substantiate this statement as far as wood is concerned. The few data that are available are given in Table 2 (*19*); they are merely the dielectric constants for woods of unknown moisture content.

TABLE 2.—*Dielectric constants (specific inductive capacities) of wood of unknown moisture content*

Species	Dielectric constant	
	Parallel to grain	Perpendicular to grain
Red beech [1]	2. 51–4. 83	3. 63–7. 73
Oak	2. 46–4. 22	3. 64–6. 84

[1] Possibly a European wood.

EFFECT OF MOISTURE CONTENT ON THERMAL CONDUCTIVITY

Figure 7 gives a typical example of the findings of Griffiths and Kaye (*2*) on the effect of moisture content on the thermal conductivity of wood. The range in moisture content that their experiments embraced was too small to show whether the effect of absorbed water is different from that of free water.
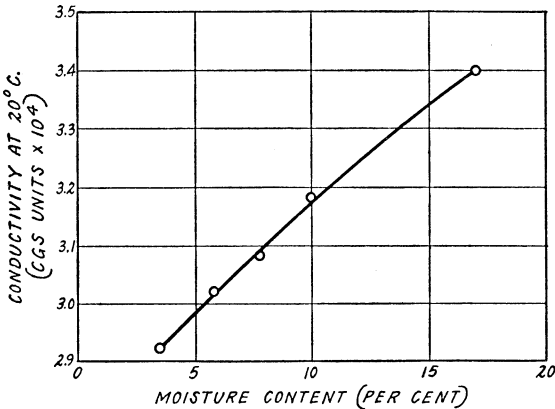
FIGURE 7.—The effect of moisture content on the thermal conductivity of spruce

In addition to the effects of moisture the same investigators found that, over the range in moisture content shown in Figure 7, the longitudinal thermal conductivity is about twice that of either of the transverse conductivities, while the radial conductivity is usually 5 or 10 per cent greater than the tangential.

THE FIBER-SATURATION POINT

The term "fiber-saturation point" was first used, by Tiemann (*26*), to designate the moisture content at which further reduction causes an increase in the strength of the wood. As other water-absorption phenomena were studied the term gradually came into use to express the more general conception of the limit of absorption of water by wood substance, and it will be used in that meaning in this bulletin. Although the fiber-saturation point has been determined by several methods, no complete and accurate study of differ-

ent species and specimens has been carried out. Figures 4, 5, and 6 indicate methods by which the fiber-saturation point may be determined; none of them, however, are entirely satisfactory.

The points where the temperature curves of Figure 4 intersect the 100 per cent relative-humidity curve indicate the fiber-saturation points at the respective temperatures. Most of these points were not actually determined—as indicated by the dotted portions, most of the temperature curves were extrapolated (by calculation) above the 90 per cent relative humidity intersections. The fiber-saturation point can not be accurately and directly determined by the method of Figure 4 because of the small capillaries (the cell cavities) existing in the wood. In a saturated atmosphere these cavities will condense moisture and consequently will give an apparent fiber-saturation point much higher than the actual value that is due to the water absorbed by the cell wall. It is possible that with thin transverse sections of wood or with relative humidities of say 99.8 per cent this difficulty could be avoided and close approximations made to the true limit of absorption. Volbehr (*31*) has reported a determination of the fiber-saturation point of pine wood made by this general method, with a result of 29.03 per cent, but he does not describe the details of his technic.

The relation between moisture content and strength shown in Figure 5 offers a method for determining the fiber-saturation point, but it is not a simple one because of the large number of observations and tests required to give accurate average results. In several series of strength tests similar to those of Figure 5, the fiber-saturation points of a number of woods have been found to vary between 20 and 31 per cent in average values, with an even greater range between individual values (*26*, *27*). This wide variation in the results obtained in the past indicates a lack of suitability in this method for determining the fiber-saturation point; the curves of Figure 5, however, may show that increased refinement in test and work-up will give more nearly consistent results. On the other hand, there is some evidence that even within the same species the indicated fiber-saturation point may vary with the particular strength value investigated.

Figure 6 shows some results obtained by a rapid and fairly accurate method for determining the fiber-saturation point. Thin sections of wood were used so that the desired moisture content could be readily obtained without a moisture gradient. The break in the curve that presents the relation between moisture content and electrical conductivity is not sharp enough to give an accurate determination of the fiber-saturation point, but the results plotted in Figure 6 show that the break comes at 30 per cent $\pm$ 1 per cent.

The relation between swelling and moisture content has also been used for determining the fiber-saturation point. Theoretically there should be no shrinkage of green wood on drying until the fiber-saturation point is reached, but here also the effects of the wood structure and of unequal moisture distribution prevent accurate determinations by this method (*13*).

It is evident that many more careful and precise determinations are needed to give conclusive and detailed information on the fiber-saturation point of wood; they should cover such matters as the

variation in different species, the variation at different temperatures, and the variation after different treatments. The few existing determinations show too much divergence to be satisfactory.

REVERSIBILITY OF ABSORPTION

Very little is known about the reversibility of the absorption of water by wood. Although this absorption seems to be substantially completely reversible there are indications that drying wood to a very low moisture content or subjecting it to elevated temperatures (6) permanently changes the value of the equilibrum moisture content. Further, like pure cellulosic fibers, wood has a hysteresis effect, with a difference in the equilibrium values when absorbing and when giving off moisture (1, 14, 30).

ABSORPTION OF LIQUIDS OTHER THAN WATER

Even less is known about the absorption of liquids other than water, although there are a few scattered data on the subject. The relative swelling effects of different liquids on dry birch wood have been determined by Hasselblatt (3) as shown in Table 3. The liquids are arranged in the table in the order of decreasing polarity, and the amount of swelling is seen to decrease in the same order. By an indirect method Stamm found in the absorption of liquids of various polarities consistent differences that are similar to the differences indicated in Table 3 (22). Dunlap has reported that turpentine and coal tar creosote give heats of absorption of 2.3 and 5 calories per gram of wood, in comparison with the 14.6 to 19.6 calories for the heat of absorption of water. Wieben[8] found that white spruce absorbed about 4.5 per cent by weight of kerosene from air saturated with kerosene vapor and 5 per cent of xylol under a similar condition. Theses figures may not be the maximum amount because the tests were not run to equilibrium, but they are probably somewhere near the equilibrium value.

TABLE 3.—*Tangential swelling of birch (dried at 110° C.) in various liquids*

Liquid	Percentage increase over original dimension	Liquid	Percentage increase over original dimension
Water	13.6	Turpentine	1.8
Glycerin	13.1	Benzol	.7
Ethyl alcohol	9.4	Carbon bisulphide	.8
Propyl alcohol	9.5	Decaline	.3
Acetone	9.1	Petroleum	.3
Ethyl ether	4.4	Ligroin	0
Chloroform	4.2		

There are no quantitative date available on the subject of the effect of the absorption of liquids other than water on the physical properties of wood. Tiemann has shown, however, that air-dry wood (about 12 to 15 per cent moisture content) soaked in turpen-

tine, kerosene, or coal tar creosote gives decreased strength values, although the values are not decreased to the same extent that they are when the wood is soaked in water (*26*).

DYNAMICS

This bulletin has already discussed the structure of wood and the static relations between liquids and the cell-wall substance of wood. In brief résumé, wood in general is made up largely of longitudinally arranged hollow elements from 0.5 to 8 mm. in length, from 0.003 to 0.4 mm. in inside diameter, and from 0.002 to 0.04 mm. in thickness of wall between two adjoining cavities. These elements, either tracheids, fibers, or vessels, communicate with one another by means of extremely small but numerous openings through thin membranes; the openings, which are of unknown shape, have the effective size of circular apertures 11 mμ to 184 mμ in diameter for softwoods, and probably are substantially the same for hardwoods. In addition there is another and much smaller system of radially arranged cells, shorter than the fibers, which communicate with one another and with the adjoining longitudinal fibers through apertures of unknown shape and size that probably are similar to those between the fibers. The walls of which this structure of intercommunicating passages is built up are composed of a reversible aqueous jelly that can absorb, with swelling, about 29 per cent of its weight of water and less amounts of other liquids. With the preceding information concerning this structure and the properties of the substance composing it as a part of the basis, the conditions under which liquids may exist in wood and move through wood may now be discussed.

Liquids may exist in wood in three forms: (1) As free liquid in the cell cavities, (2) as bound liquid in the cell walls, and (3) as vapor in the cell cavities. Since the vapors in wood under practical conditions are always mixed with some gas, that is the only condition of vapor existence which will here be discussed. The free liquid can exist only when the adjacent wood substance is at the fiber-saturation point, but the other two forms occur at all values of moisture content (except that the vapor form will be absent in cells completely filled with liquid). Movement of free liquid can therefore take place only above the fiber-saturation point, and bound liquid and vapor can diffuse in response to variation in concentration or in vapor pressure only below the fiber-saturation point. All three movements can take place simultaneously, however, in different parts of the same small piece of wood. Certain general physical laws govern fluid movements of these types and with their aid it may be possible to correlate the known structure and properties of wood with the existing experimental data and thus obtain some evidence on the probable mechanism of the movement of liquids through wood, especially under the conditions that prevail in the practical processes of impregnation and drying.

IMPREGNATION BY PRESSURE

The impregnation of wood by liquids under pressure, as in the preservation process, is probably the simplest case of the movement

of a liquid in wood, because it consists almost entirely of the movement of free liquid. If the impregnating liquid is an oil that is only slightly absorbed by the cell wall, the bound-liquid movement will be negligible. If on the contrary it is a water solution, since the cell walls are already partly saturated the only bound-water movement will then be merely that required to complete the saturation by absorption from the free water as it comes in contact with the partly saturated cell wall. In either instance the vapor movement will be negligible in comparison with the amount of free-liquid movement. It is permissible, therefore, to consider impregnation as the movement of free liquid only. If it is such, the movement should follow the well-known laws governing the flow of liquids through small tubes. A simplified expression of these laws is given by Poiseuille's equation,

$$\frac{V}{t} = \frac{\pi r^4 P}{8 \eta l} \tag{1}$$

in which V represents the volume of liquid that has flowed, t the time of flow, r the radius of the tube, P the pressure, η the viscosity of the liquid, and l the length of the tube, all in centimeter-gram-second units. The equation is not directly applicable to the impregnation of wood by liquids because it expresses the conditions of liquid flow through tubes already filled with liquid, while the commercial impregnation of wood both involves the flow of liquid into empty tubes and includes a variation in the value of l. The mathematical relationship between these two types of flow will be developed later in this report. Before this is done, however, it will be necessary to discuss other variables, not used in equation (1), that may affect the flow of liquids through or into wood.

LOCALIZATION OF RESISTANCE TO FLOW; IMPACT TURBULENCE

As already indicated, the open passages through wood are not capillary tubes of constant diameter as required by Poiseuille's equation but are instead a series of discontinuous capillary tubes (the cell cavities) communicating through numerous orifices very much smaller than the tubes themselves. The orifices are so small, comparatively, that practically all the resistance to the flow of liquids is localized in them, and hence the resistance to flow in the cell cavities may be considered negligible (21). The sudden change in diameter of the passages, from an orifice to a cell cavity, brings in another variable, impact turbulence, not included in Poiseuille's equation. The effect of impact turbulence can be computed from Couette's modification (22) of Poiseuille's equation. Under the average conditions prevailing in the impregnation of heartwood, impact turbulence is negligible. Even under the most exceptional conditions that might occur locally or temporarily in the flow of the impregnating liquid through the cell cavities of heartwood the maximum correction to be applied to computations from equation (1) would be only about 1.6 per cent. Therefore the effect of impact turbulence need not be considered in the further discussions of impregnation.

EFFECTS OF CAPILLARY FORCES

When liquid is entering either an empty capiilary or a gas-filled one the flow is affected by the surface tension of the liquid at its entering surface, which for the gas-filled capillary is the boundary between liquid and gas. The effect of the surface tension may be expressed quantitatively in terms of pressure tending to cause flow, and the general phenomenon of surface tension modified by size of capillary is often called "capillary pressure." Since this pressure may be exerted either toward or away from the surface, depending on the shape of the surface film, it may be either a positive or a negative pressure in so far as the internal pressure of the liquid is concerned. It is often expressed, however, as a positive pressure acting in one direction or the other. The discussion immediately following and also the discussion of Figures 11 to 14 make it desirable to restate here the preceding well-known facts.

Under the conditions postulated for the Poiseuille equation no capillary forces are acting. Such forces, however, not only may act but may also become important when the liquid is entering capillary spaces in wood that are filled with air. If the liquid wets the wood the capillary forces tend to pull the liquid into the empty spaces; that is, the resultant of these various forces acts in the same direction as the pressure applied to the liquid from the outside of the piece. The capillary pressure varies inversely as the radius of curvature of the meniscus, which in turn depends upon the radius of the capillary, and the cell cavities are small enough to give, with water as the liquid, about half an atmosphere of capillary pressure—a value not large in comparison with the external pressures applied in practice. The capillary pressures caused by meniscuses in the orifices in the pit membranes, on the other hand, may be greater than 50 atmospheres, although they are practically ineffective in assisting to force liquid into the wood on account of the extreme thinness of the membranes and the correspondingly short distances through which the high values are active. In fact the pit membranes may actually retard the capillary rise of liquid into wood on account of the large angle of the surface film just after the orifices have become filled with liquid.

If the liquid does not wet the wood, the resultant of the capillary forces acts in the direction opposite to the direction for water, that is, against the flow of the liquid into the empty spaces. In this case, however, it is the small, short capillaries of the pit membranes that are most important, since they determine the minimum force required to cause the initial flow of liquid into a cavity. With a liquid that does not wet wood a pressure as high as 50 atmospheres may be required to overcome the capillary pressure and cause a flow from one cell cavity to another.

As long as the liquid wets the wood, therefore, the effect of variation in surface tension is not important in modifying the externally applied pressure, but whatever its surface tension a liquid that does not wet the wood can be forced through the small orifices only by extremely high pressures. Although the liquids used for treating wood do wet the wood under normal conditions, yet there may be

temporary and localized resistance to wetting caused by extremely small surface deposits of materials not wet by the liquid. A strictly analogous occurrence is often noted in the flow of water into glass capillaries that are not perfectly clean. If such resistances to wetting were localized in the small orifices they would be important in preventing, or at least in retarding, the flow of the liquid.

<div align="center">TRAPPED AIR</div>

During the impregnation of wood the air in the cavities may be trapped in two different ways, which have different effects on the impregnation process. In the more apparent way the air occupies the central, untreated portion of the piece, and in the more important one it forms bubbles in the cell cavities that are otherwise filled with the treating liquid. The first of these bodies of trapped air is not likely to be of appreciable moment in its effect on impregnation. Even if no air were trapped as bubbles and all the air formerly in the treated portion of the piece were displaced toward the center, its pressure would thereby be raised only in the ratio of the volume of the air displaced to that of the air previously in the untreated portion. For example, if one-half the piece is treated and all the air is therefore compressed into one-half the volume it originally occupied, the pressure of the compressed air is only doubled, and if it were at atmospheric pressure at the start it would then be at a pressure of only two atmospheres. An increase in internal pressure of an atmosphere or so is small in comparison with the external pressures of 7 to 15 atmospheres commonly applied in practice. Furthermore, the amount of air trapped as bubbles correspondingly decreases this effect. Usually the treating liquid penetrates less than one-half the piece, as one more consideration, and in the experimental data to be considered later in this bulletin less than one-half was thus penetrated.

The effect of air trapped as bubbles in the liquid is much more complicated. That this kind of air entrapment does take place, however, is easily established. It is proven by the "kick back" of the liquid, the reversed flow of liquid out of the wood that occurs when the pressure is released after the impregnation treatment has been finished. Although it may be thought that the kick back is caused by the air that has been compressed in the untreated, central portion of the piece, this can not be the fact because the air compressed in the center of the piece can not expand further than to the nearest small orifices. When the liquid has retreated until the dividing surfaces between the air and the liquid lie within these orifices, the capillary pressure resisting further retreat may be as high as 50 atmospheres, a pressure far greater than that of the compressed air. The kick back at ordinary commercial treating pressures must be due, therefore, to the combined effect of the expansion of many small air bubbles trapped in the liquid.

The kick back caused by the expansion of trapped air is occasionally accompanied by a similar effect caused by the expansion of the wood itself upon the release of the applied pressure. This effect is noticeable chiefly in species of relatively low mechanical strength that are resistant to impregnation treatment and when

high temperatures and pressures are used. Since only the total kick back can be measured, it is difficult to estimate the individual amounts that are due, respectively, to each of the two possible causes.

The air confined in the central, untreated portion of the piece affects the impregnation directly in that its pressure is substracted from the applied pressure to give the total effective pressure. The effects of the air trapped as bubbles are much more involved and are correspondingly difficult to estimate, especially the immediate effects as distinguished from the later kick back. If there were no change in the pressure to which these bubbles are subjected they would have no effect on the amount of flow. Since, however, the bubbles are subjected to increasing pressures and therefore diminish in size as the impregnation proceeds, the cell cavities in which air is trapped are not filled to their final capacity when the liquid enters them initially but continue to fill with liquid throughout the course of the impregnation process. The quantitative aspects of this effect will be discussed later in this bulletin.

FLOW OF IMPREGNATING LIQUID

Before discussing the effect of such variables as viscosity and pressure on the amount of liquid injected into wood in the impregnation process, it is desirable to develop the mathematical relationship between the type of flow covered by equation (1) and that which takes place during treatment. This can readily be accomplished after making the simplifying assumptions that the structural conditions of the wood remain substantially unchanged during impregnation and that the dimensions of the different cell cavities and the number and dimensions of the communicating passages between the different cell cavities are the same throughout the wood. Although the last assumptions are obviously untenable, the flow through a large number of cavities and communicating passages, even though the channels have widely varying dimensions, would be much the same as that through equivalent channels having constant dimensions, and the assumptions are therefore justified for their present purpose.

The results of experiments in wood impregnation are naturally expressed in terms of total amount of liquid absorbed or in depth of penetration. Such terms evidently bear a relationship to the V, volume, in equation (1), but the exact nature of the relationship must be ascertained. Washburn (32) has already developed such a relationship for capillaries of uniform bore, but his equation does not apply under the conditions under discussion because, as already pointed out, the flow of liquid into wood may be safely considered as the filling of successive reservoirs (the cell cavities) through extremely restricted and short communicating orifices (the pores in the pit membranes), the resistance to flow as expressed by r and η being located practically entirely in the orifices. The flow of the liquid during impregnation can therefore be considered as a series of discontinuous flows, the conditions remaining constant while one set of cell cavities is being filled and the resistance increasing stepwise by a practically constant amount as each set of cell cavities is filled and the liquid begins to flow through the next set of orifices.

Accordingly, if it takes one unit of time to fill the first set of cavities through one set of orifices, it will take two units of time to fill the second set of cavities, since for the second filling the liquid must flow through two similar sets of orifices in series; the third set of cavities will require three units of time, and so on.   If, then, y is the depth of penetration, b the dimension of a cell cavity in the direction of the flow, x the time required to penetrate the depth y, and a the time required to fill the first cell, when $y/b=1$, $x/a=1$; when $y/b=2$, $x/a=3$; when $y/b=3$, $x/a=6$; and so on.   The relation between y/b and x/a is therefore given by the equation

$$\frac{x}{a} = \frac{y}{b}\left(\frac{\frac{y}{b}+1}{2}\right),$$

or

$$x = ay\left(\frac{y+b}{2b^2}\right) \tag{2}$$

Equation (2) requires that every row of cells be either completely filled or at least filled to the same extent, and that the final maximum filling of each row take place before the next row begins to fill.   Air bubbles trapped in the cell cavities prevent the individual fulfillment of both of these requirements, (1) because, although each cell may be originally filled to the same extent (to the stage where the entrapment of air is finished), the final subsequent compression of the trapped air and the corresponding additional amount of entering liquid that remains in the cell will vary according to the pressure on the liquid finally attained, and (2) because as the trapped air is compressed the cell continues to fill with liquid after the liquid has begun to flow into the cells beyond.   Although the presence of trapped air thus destroys the actual quantitative relationship shown in equation (2) between the times required to fill the first row of cells and the subsequent rows, yet after the first two or three rows of cells have been filled the additional time required to fill each successive row becomes constant (to less than 1 part in 200) for any given piece, and this individually constant value is a function of the time required to fill the first row.   This statement is introduced without proof because the development of the formulas and the computations on which it is based would take more space than the subject merits.   If the statement is accepted, then equation (2) may be used exactly as it stands although a will then no longer represent the mathematically exact time required to fill the first cell but instead a function of that time, which has a practically constant value for a given case.

No attempt will be made to apply equation (2) to the experimental wood-impregnation data on the relation between time and penetration; it will be used only in applying equation (1) to the data on the effect of pressure and of viscosity.

MacLean's curves showing the relationship between time and penetration (7) are of the same general type as those given by equation (2) except for the considerable amount of absorption recorded as occurring at the very beginning of the impregnation, even before the maximum pressure has been attained.   This rapid absorption at

the start is undoubtedly due to checks and ruptured cell walls that allow certain cavities to be filled without the passage of the liquid through apertures as small as those between the cell cavities. After this abnormally rapid first absorption, MacLean's curves can be closely duplicated by means of equation (2) with properly chosen values of a and b. The duplications are not exact, it is true, probably because the conditions assumed to be constant in the derivation of the equation were not actually constant during the experimental impregnations. The theoretical and experimental curves are so close, however, that the theoretical can be safely used in combination with equation (1) to deduce the effects of pressure and viscosity on penetration for comparison with the experimental results.

EFFECT OF PRESSURE ON PENETRATION

For all practical purposes y, the penetration, in equation (2) may be considered to vary inversely as the square root of a, the time required to fill the first cell. Although this relation between a and y, which is affected by the value of the constant b, is never strictly accurate, when y is large in comparison with b, as it always is except at the very beginning of the impregnation, the inaccuracy is negligible. According to equation (1) the time a required to fill the first cell should vary inversely with the pressure p. Therefore, other conditions remaining constant, the penetration y should vary as the square root of the pressure p. Yet MacLean's figures showing the effect of pressure on penetration do not give exactly such a relationship. The effect of pressure on penetration is not consistent in his different experiments; in general, however, the penetration he obtained varies more nearly directly with the pressure than with the square root of the pressure. The universal laws governing the flow of liquids in capillaries can not become suddenly inoperative in the impregnation of wood, and therefore some reasonable explanation of this apparent peculiarity must be sought.

If, as has been indicated in the previous discussion, the openings between the cell cavities are located in the very thin pit membranes, it seems reasonable to assume that pressure may cause a stretching of the membrane with consequent increase in the size of the openings. Hence all the conditions affecting the rate of flow, other than pressure, may not have been constant in the experiments. Rather, the size of the openings may also have varied, and may have varied as some function of the pressure. That this explanation is reasonable is further indicated by the fact that the same mechanism may be used in accounting for the observed effects of steaming the wood just prior to impregnation. Common practice in commercial plants is to steam the wood in order to increase the ease of penetration, and since steaming is known to soften the wood, making at least the macroscopic units of the wood substance more plastic, it probably increases the effect of pressure on the stretching of the membranes and therefore on the size of the openings.

EFFECT OF VISCOSITY ON PENETRATION

According to equation (2), the penetration should vary inversely as the square root of the time required to fill the first cell, and accord-

ing to equation (1) the time required to fill the first cell should vary directly as the viscosity. All other factors affecting impregnation being constant, the penetration should therefore vary inversely as the square root of the viscosity.

The experimental data showing the effect of viscosity on penetration are very meager. In most of MacLean's work (*7, 8,* and *9*) on the effect of viscosity on penetration he obtained variation in viscosity by variation in temperature. The effect of viscosity alone, therefore, can not be determined from these data. In a few of his experiments, however, temperature was held constant and variation in viscosity was obtained by using mixtures of coal tar creosote with various proportions of petroleum oil. Four different petroleum oils were used, although only one at a time was mixed with the creosote. For the mixtures of creosote with any one oil, the relation between viscosity and penetration corresponds fairly well to the theoretical relation.

$$\text{penetration} = \frac{\text{constant}}{\sqrt{\text{viscosity}}},$$

although the constant is different for the different oils. Even when the results for all four oils are plotted together, there is a rough correspondence to a straight-line relationship between the penetration and the square root of the reciprocal of the viscosity. It may be concluded, therefore, that the experimental data, within the limits of their inconsistencies, confirm the deduction that the effect of viscosity on penetration in wood impregnation is what would be expected from the laws governing the flow of liquids in capillaries.

DIFFUSION CAUSED BY DIFFERENCES IN MOISTURE CONTENT

There are no data on the diffusion in wood of either pure vapor or pure bound liquid, and a detailed discussion of the diffusion equations that might apply is therefore unnecessary. It is of interest, however, to review the attempts that have been made to apply diffusion equations to experimental data obtained in the drying of wood. Tuttle (*28*) and later Sherwood (*18*) applied diffusion equations to the rate of drying of wood and found a good concordance of calculated and of observed results. In both instances, however, the wood was above the fiber-saturation point at the beginning of the experimental work, and the apparent success of the application of the diffusion equation proves only that the probably complicated mechanism actually in operation happened to have a resultant the same as that of the assumed simple mechanism; the success does not prove that the mechanism of the moisture movement corresponds to the assumptions of a simple diffusion. In fact the available information already reported herein demonstrates that this can not be so. The water existing in wood above the fiber-saturation point is free water, and free water has no properties that would cause it to diffuse from a point of higher to a point of lower concentration, as required by the diffusion law. Hence, in order to obtain details on the mechanism of moisture movement in wood through proper application of the diffusion laws it is necessary to use simplified cases in which the three different mechanisms that are possible in that movement may not all be in action at the same time.

The problem is simplified and the interpretation of results is less difficult when the experiments are conducted on wood below the fiber-saturation point so that instead of three there are only two possible ways of moisture movement—as vapor and as bound liquid. Still-well (*24*) and Martley (*11*) have studied the diffusion of water through wood below the fiber-saturation point and have further simplified the interpretation by carrying on the diffusion at a constant rate, that is, with a constant high relative humidity on one side of a piece of wood and a constant low relative humidity on the other side. Under these conditions the distribution of the moisture, the moisture gradient in the direction of flow, may be expected to give some information on the mechanism of the diffusion. The usual diffusion equation assumes a driving force proportional to the differences in concentration of the diffusing substance. If this assumption held for wood, with no other variable affecting the rate of diffusion, and if the moisture diffusion through wood were entirely as bound liquid, the moisture gradient set up at the steady state should be a straight line as shown in Figure 8, A. If, on the other hand, the diffusion were entirely in vapor form, the gradient of vapor pressure should be a straight line at a steady state, but the graph representing the

FIGURE 8.—Theoretical moisture gradients in wood at a steady state: A, When the moisture moves as bound water; B, when the moisture moves as vapor

different moisture-content values of the wood in equilibrium with these uniformly varying vapor pressures would not be a straight line. Instead, the moisture gradients in equilibrium with a straight line of vapor pressures would have a form similar to the curve in Figure 8, B. The assumption that the driving force is proportional to differences in vapor pressure is undoubtedly true for pure vapor diffusion, but there is no evidence that the driving force is proportional to differences in moisture content in bound-water diffusion. On the contrary, the available evidence is opposed to such an assumption. It has been shown under the heading Statics (figs. 3 and 4) that the intensity of absorption of water by wood, as measured by heat of absorption and by diminution of vapor pressure, decreases greatly over the range from dry wood to the fiber-saturation point, and it might be expected that the diffusion constant would vary in the same

manner. If this were so the moisture gradients caused by the diffusion of bound water should also resemble Figure 8, B.

Stillwell (24) found that the moisture gradients did not correspond closely to either of these assumptions but were more like Figure 8, A, or in some cases even convex from above. Nor did the rate of diffusion give any definite evidence of the mechanism. His work, however, was described as only preliminary in character, and certain experimental difficulties in the control of conditions were pointed out as affecting the results to such an extent that quantitative conclusions could not be drawn.

Martley (11), also making his experiments at the steady state, found that all his moisture gradients were curves convex from above and approached tangency to the horizontal at high values of moisture content, indicating that diffusion is more rapid at the higher values of moisture content. His experiments, therefore, do not indicate which diffusion mechanism, vapor or bound water, is preponderant in the drying of wood below the fiber-saturation point, but they do show that, whatever the mechanism, and whether difference in vapor pressure or difference in moisture content is the driving force, the diffusion is not proportional to the driving force alone. It varies also with the moisture concentration; this concentration may be that in the wood substance for the diffusion of bound water or that (partial pressure) in the air in the cell cavities for the diffusion of vapor. The same kind of a moisture gradient has been noted with drying soap (18), where the water is all bound water, and also in the diffusion of water through rubber (17), where the movement appears to be largely in the form of vapor. The fact that there is a variation with concentration, therefore, does not indicate any preference for either of the two possible forms of water movement.

Undoubtedly both forms of diffusion, as vapor and as bound water, are taking place at the same time in the drying of wood below the fiber-saturation point. The only question concerns the relative speed of the two forms. This can be determined by measuring the effect of some variable that can affect only one form of the diffusion or by adding a variable that can be affected by only one form. Studies of this kind are already under way at the Forest Products Laboratory. There is also another experimental method for differentiating between these two forms of moisture movement in drying; it is based on the fact that vapor diffusion requires heat for the evaporation of moisture in the interior of the wood, while bound-water diffusion requires heat for evaporation only at the surface. The temperature gradients in wood drying below the fiber-saturation point, therefore, may throw some light on this subject. Another suggested method is to study the rate of drying of wood saturated with a volatile liquid not absorbed or only very slightly absorbed by the cell wall, so as to exclude or at least minimize any diffusion as bound liquid.

MOVEMENT OF LIQUID ABOVE THE FIBER-SATURATION POINT

It has already been shown that the water occurring in wood above the fiber-saturation point is free water and that differences in moisture content above the fiber-saturation point, such for instance as between 40 and 50 per cent, do not in themselves develop any potential that can cause a flow from the higher to the lower concentration.

Yet there is evidence that free water moves in wood during the drying process. The main evidence, and all that needs to be considered here, is found in determinations of the moisture gradients at different stages of drying. If there were no movement of free water during drying the moisture gradients at successive periods would be as shown in Figure 9—curves A, B, and C, in order. All the movement of moisture toward the drying surface would then lie in portions of the piece below the fiber-saturation point, and the sharp break in the moisture content between the fiber-saturation point and the original moisture content would persist but would gradually move away from the drying surface. Such curves are in fact obtained with certain kinds of wood. On the other hand, certain other kinds of wood furnish moisture gradients similar to those of Figure 10, in which the original moisture content is seen to drop considerably before the fiber-saturation point is reached. The movement of free water is the simplest explanation of this type of moisture-distribution curve.

Such a movement of free water during drying can be readily explained by the application of the information that has already been presented on the structure of wood and on wood-water relationships. Fortunately it is not necessary to assume that either vapor diffusion or bound-water diffusion is the more rapid in order to make this explanation. The movement toward the drying surface in that part of the piece of wood below the fiber-saturation point may
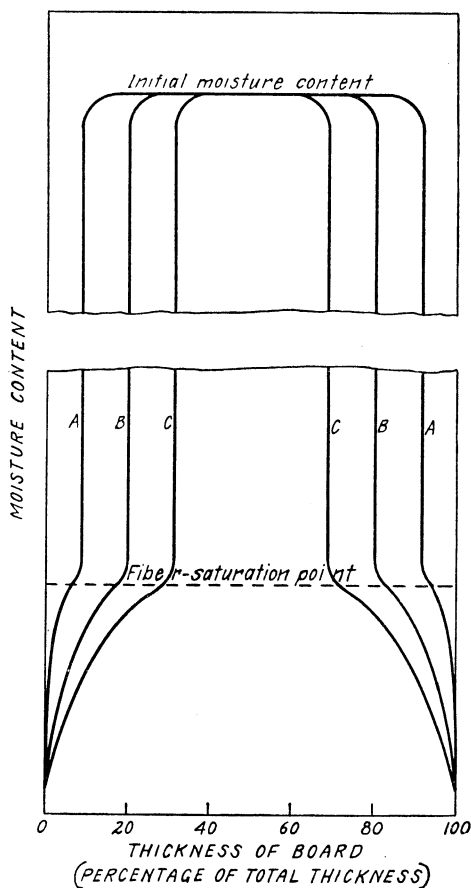

FIGURE 9.—The moisture-gradient in wood at three stages of drying when there is no movement of free water: A, at an early stage in drying; B and C, at successive later stages

be largely due to either of these mechanisms and yet the general effect on free-water movement will be the same. This explanation of free-water movement does in fact present a fairly complete and definite picture of the details of moisture movement during the drying of wood. It is not yet possible to give a quantitative treatment of the subject, but the following conception seems to fit the known facts and to furnish an acceptable presentation of the various mechanisms involved.

In addition to the foregoing it is only necessary to consider briefly the evaporation from the free surface of water in a capillary before developing the subject in connection with the drying of wood. As explained under the heading, Effect of Capillary Forces, capillary tension and pressure vary inversely with the radius of the capillary, and the same principle applies to a small bubble of air or othe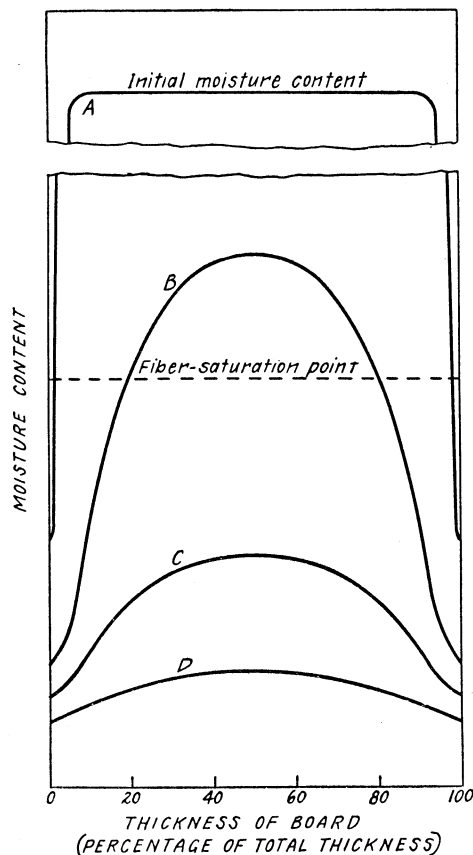r gas in a liquid. If, therefore, we consider a capillary of irregular cross section, Figure 11, filled with water except for a bubble, b, the system is in equilibrium only when the radius of the tube is the same at a and c and, if the gas in b is at atmospheric pressure, when the radius of b is also the same. If now evaporation of water takes place at a the retreat of the meniscus, m, toward a_1, with constantly decreasing radius of the tube, produces a constantly increasing capillary tension and, therefore, the meniscus n moves toward c_1, its radius always being equal to the radius at the other end of the tube. Meanwhile, with the capillary tensions at the ends of the tube increasing, the bubble b expands until the gas and vapor pressure within the bubble plus its capillary pressure are equal to the capillary forces at the ends of the tube plus the atmospheric pressure; the pressure within the bubble decreases as the bubble expands. With further evaporation at m this procedure will continue until the minimum radius is reached at a_1. Then, if a_1 is smaller than c_1 the meniscus n will continue to retreat toward a_1, and the evaporated surface will move forward and back between a_1 and the end of the tube, keeping m and n always of equal size until all the water in the tube is evaporated. If a_1 is larger than c_1, the meniscus n will not retreat beyond c_1, but instead m will continue to move toward n, until evaporation is complete. The presence of the bubble b does not materially affect the procedure under the conditions shown in the figure, but, if the minimum radiuses near the ends of the tube are

FIGURE 10.—The moisture gradient in wood at four stages in typical kiln-drying when there is a movement of free water: A, at a very early stage in drying; B, C, and D, at successive later stages

very small in comparison to the radius of b, sufficient capillary force may be developed to expand b very considerably. In fact, the minimum radiuses may be so small that the capillary forces will be greater than the tension of the liquid in the surface film of the bubble b, in which event m and n will both remain stationary while b expands until the tube is emptied of liquid water.
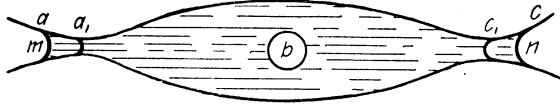

FIGURE 11.—A capillary tube of nonuniform bore, with a bubble of entrapped gas: a, One aperture; a_1, position of minimum radius of aperture a; b, a bubble of entrapped air or other gas; c, the other aperture; c_1, position of minimum radius of aperture c; m, meniscus at aperture a; n, meniscus at aperture c

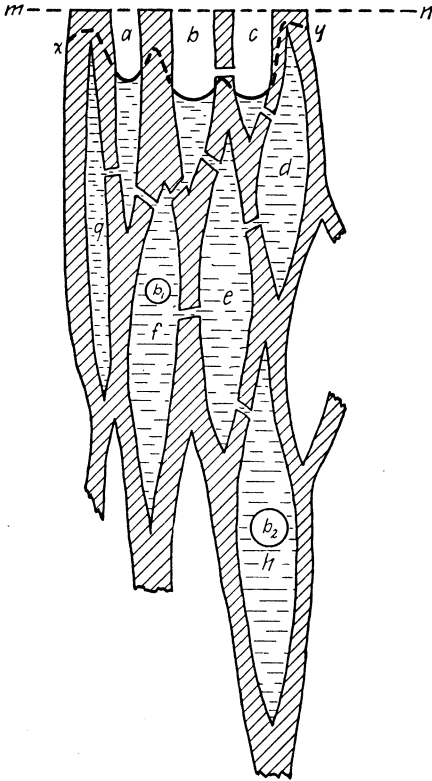FIGURE 12.—An early stage in the drying of an idealized wood structure: a, b, c, d, e, f, g, and h, Fiber cavities in an idealized wood structure: b_1 and b_2, bubbles of entrapped air or other gas; mn, exterior surface of the piece of wood; xy, surface of the liquid in the cavities from which evaporation takes place

APPLICATION OF PRINCIPLES TO A SIMPLIFIED STRUCTURE

For the application of the preceding principles to the drying of wood we may use an idealized and simplified structure (figs. 12, 13, and 14) that resembles wood in all the details essential to this discussion. The cells selected for illustration have an inside diameter of about 0.01 mm. and the orifices connecting them have a diameter of about $70m\mu$. In Figure 12 all cell cavities when drying started were full of water, except f and h, which contained air bubbles. Evaporation from the surface of the wood mn lowers the water level in the cells a, b, and c, and at the same time the walls begin to dry out from the line mn downward. Further evaporation brings the water level down to the positions shown in Figure 12. Other evaporation of water is probably also taking place from the cell walls into the cell cavities, as indicated by the line xy, which marks the limit of fiber saturation in the cell walls. There is a definite capillary tension at each of the meniscuses in a, b, and c; these tensions, however, can have an effect in moving liquid water only when the curvature of any meniscus or bubble surface in the intercommunicating system is larger than the curva-

tures in *a*, *b*, and *c*. The level in *a* is shown as higher than the levels in *b* and *c* on account of the greater capillarity in *a* (*a* is slightly smaller than *b* and *c*). If the bubble in *h* has a diameter greater than the diameter of the meniscus in *a*, it will expand after evaporation from the surface at *x* until equilibrium is restored, in accordance with the action described in connection with the bubble in Figure 11.

Continued evaporation will finally bring about the situation indicated in Figure 13. Here the cells *a*, *b*, and *c* no longer contain water, and there is a meniscus across each of the orifices leading inward from these cells. On account of the great increase in the capillary forces in these small orifices over the forces previously exerted by the larger meniscuses in the cell cavities, the evaporating surface will tend to remain stationary within them as long as there are larger surfaces from which the water can flow to replace the evaporated water. At the same time there is evaporation of bound water into the cell cavities of *a*, *b*, and *c*; the bound water is supplied by diffusion through the cell walls from the free water in contact with the other sides. The bubbles b_1 in *f* and b_2 in *h* had previously been in equilibrium with the capillary forces exerted by the meniscus in *a*. Now they must come into equilibrium with the conditions set up by the much smaller meniscuses in the orifices between the cell cavities. The water evaporation along the line *xy* is supplied by the expansion of the bubbles, and the internal tension in the body of the water gradually increases, for a time, as this evaporation proceeds. The ex-
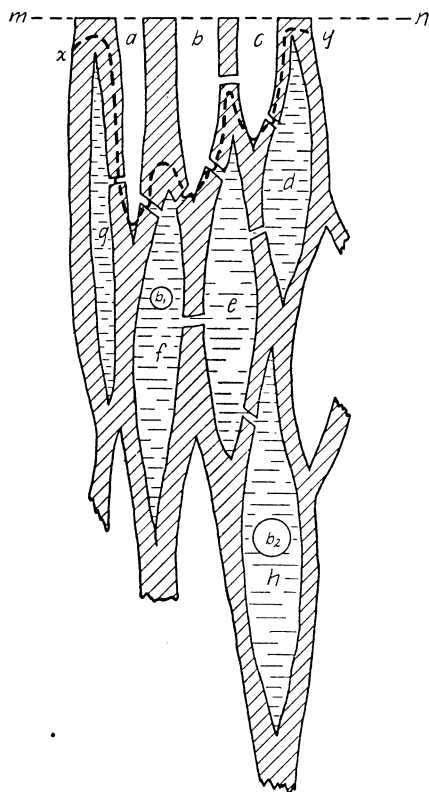

FIGURE 13.—A second stage in the drying of an idealized wood structure: *a*, *b*, *c*, *d*, *e*, *f*, *g*, and *h*, Fiber cavities in an idealized wood structure; b_1 and b_2, bubbles of entrapped air or other gas; *mn*, exterior surface of the piece of wood; *xy*, surface of the liquid in the cavities from which evaporation takes place

pansion of the bubbles during this stage is accomplished by expansion of the air contained in them and by evaporation into them of water from their surface films. Finally, however, the increasing vapor pressures of the water in the surface films become equivalent to the tension conditions in the body of the liquid, and then the bubbles continue to expand without further changes in liquid tension. This stage is reached by b_2 sooner than by b_1, since the size of the bubble and hence the vapor pressure in the surface film of b_2 is greater. The bubble b_2 expands until it fills the

cavity h, all the water passing upward into e. This leaves a meniscus in the orifice between e and h, which will remain stationary as long as there are larger surfaces anywhere in the system to be moved first. The bubble b_1, being larger than any of the meniscuses now in the system, will expand under increasing tension until it reaches the second stage described for bubble b_2 and will then expand further at constant liquid tension until it fills f. Since there is now no water to sustain them the films in the orifices between a and f, and f and b will completely evaporate, and the pressure in f will be made normal by the entrance of air from a and b. The condition shown in Figure 14 is now reached. Only the three cell cavities d, e, and h are left active in the dead-end system, and the next development depends on the relative size of the orifices at which there are meniscuses. If the one between h and e is the largest (and is also sufficiently larger than the others to make up for the low pressure existing in h) it will be pulled into e, and the water in e will pass out p a r t l y through d and partly through the cell walls and orifices into b and f. If, however, the orifice between c and d is the largest of the group its meniscus will be pulled back into the cavity d, and on account of the low pressure existing in h a part of the water in d will flow through e to h until the pressure in h is again normal. Thus there is the interesting possibility of occasional flow of liquid water for a short distance in the direction away from the drying surface whenever a meniscus on the drying surface becomes greatly enlarged by being pulled back into a cell cavity.

FIGURE 14.—A third stage in the drying of an idealized wood structure : a, b, c, d, e, f, g, and h, Fiber cavities in an idealized wood structure ; mn, exterior surface of the piece of wood ; xy, surface of the liquid in the cavities from which evaporation takes place

Collapse.—During the stages of Figures 12 and 13 the meniscuses between the cell cavities are not required to exert their maximum capillary tensions. Whenever a condition similar to that shown in Figure 14 exists, however, there will be a great mechanical stress in the walls of the dead-end system before one of the meniscuses is pulled through its orifice into a cell cavity. With orifices of an effective diameter of 70 mμ the tension required to pull a meniscus into the cell cavity would be about 40 atmospheres. So great a
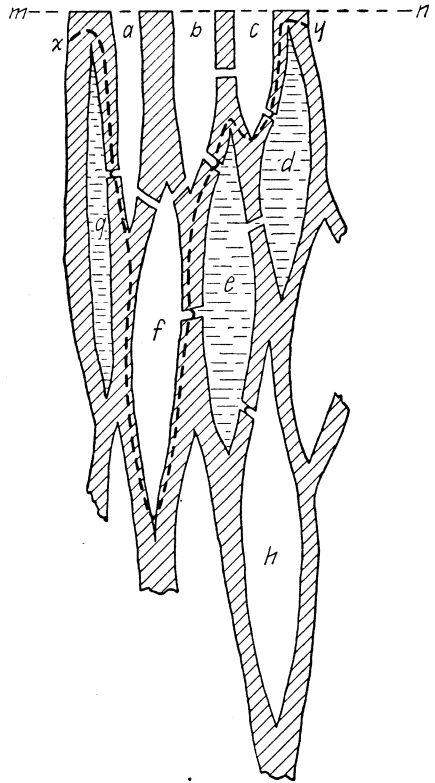
force may be sufficient in some species of wood to cause a collapse of the cell wall; such collapse is frequently observed in dried wood. Although our knowledge of the submicroscopic structure and the initial moisture characteristics of the species most subject to collapse is still too meager for a definite substantiation of this explanation of the phenomenon, all that we do know is in agreement with it.

BRIEF APPLICATION OF PRINCIPLES TO ACTUAL WOOD STRUCTURE

It is thought that the foregoing greatly simplified presentation covers the principles and the essential details of the mechanism of free-water movement during the drying of wood. Numerous details pertinent even to so simplified a presentation are not included in the discussion, but all the details omitted seem of little importance in their effect on the gross results. No attempt will be made to give any complete and detailed application of these principles to the structure of actual wood, which is much more complex than that represented in the elementary diagrams of Figures 12, 13, and 14, but a few general observations will be made in amplification and partial application of the preceding restricted discussion.

Since wood is normally made up of continuously intercommunicating passages it has no completely closed systems like that shown below mn in Figures 12, 13, and 14. The capillary force set up at the evaporating surface of an actual piece of wood, therefore, may exert an effect through a large number of cell cavities. Even in a cell cavity nearly filled with an air bubble there are probably continuous fine columns of water (resulting from the irregularities in the interior surface of the cell wall) that persist even at considerably reduced vapor and gas pressures and thus allow a flow of water through the cell. On account of the very small size of the openings between the cell cavities there is a considerable resistance even to so reduced a flow, and the openings may in certain instances be so small that the free water can not flow to the free surface as fast as it is being evaporated from the surface. In such event the meniscuses on the evaporating surface may be broken by evaporation, and the liquid surface will then recede to the next row of cells. This illustrates the manner in which a moderate variation in size or in number of the small openings between cell cavities may considerably affect the mode of drying, as indicated by the moisture gradients. Qualitatively the mode of drying is always the same—there is always some movement of free water in response to the capillary force developed at the drying surface, but this movement may extend only a few tracheids beyond the evaporating surface before the evaporating surface begins to progress inward. The result is a moisture gradient similar to those shown in Figure 9, because the distance through which free water moves in such drying is so small as to have very little effect on the gradients. Since the flow varies as the fourth power of the radius a moderate increase in the average size of the openings will cause a considerable decrease in the resistance to flow, and the movement of free water may then extend for many tracheids beyond the evaporating surface, giving gradients similar to those in Figure 10.

The picture so far presented is substantially one of movement in a longitudinal direction. The movement in a tangential direction

differs from the longitudinal only in the relative rates at which movement takes place. It should be slower because there are more membranes and hence more small openings in series per unit of distance from the drying surface than in the longitudinal direction. In the radial direction there are wood rays, which are oriented similarly to the cells in the longitudinal direction, in which the rate of movement should simulate the movement within the longitudinal cells, and consequently radial drying should partake of both longitudinal and tangential rates.

The preceding discussion of the movement of liquids in actual wood has also been limited largely to a restricted structure similar to that of a softwood without resin ducts. The presence of resin ducts or of the special vessel systems of hardwoods may greatly modify the details, but the principles and the general results will be the same.

There are no observations or experimental data on the evaporation from wood of liquids other than water so that this subject need not be discussed, but here again the general mechanism should be the same as with water.

CONCLUSIONS

Although this bulletin is essentially a review and correlation of known facts and principles it permits the drawing of definite conclusions.

Some specific conclusions are: In the impregnation of wood with liquids the effect of the viscosity of the liquid on the penetration is what would be expected from the known facts in regard to wood structure and the laws governing the flow of liquids into capillary tubes, whereas the effect of pressure on the penetration is not what would be expected, which indicates the existence of other variables not yet controlled, such for example as the effect of temperature on the plasticity of the wood. The movement of free water during the drying of wood depends on the size and the number of the openings between cavities containing water and on the proportions of air and water in these cavities.

Corollaries are: Experimental methods are suggested for determining the preponderance of vapor flow or of bound-liquid flow during drying below the fiber-saturation point. The lack of variety and of completeness in certain determinations, such as the fiber-saturation point, the size of openings in the wood structure, and structural details, especially the location and the number of pits, in different pieces and different species of wood, is pointed out.

Three conclusions are: (1) It is profitable, at an early stage in experimental work, to study the principles involved in the problem and, with the aid of all the known facts, to formulate a tentative hypothesis. (2) Mathematical formulas that fit experimental data do not necessarily give any information on what the fundamental variables are or on the relation between them; such formulas may even lead to a false conclusion in regard to the simplicity of the process. (3) In dealing with a material of complicated structure, like wood, it is necessary to know the finest details of the structure and to keep them constantly in mind in order to properly interpret experimental data or plan experimental work. These conclusions

may be considered trite and commonplace statements of prevailing opinion, but restatement and emphasis can do no harm in connection with a subject so important as efficiency in research methods.

SUMMARY

Many of the problems that occur in the drying and other preparation of green wood for use originate in the fundamental relations between wood and liquids. This bulletin summarizes the present knowledge of wood structure and of wood-liquid relations and thus serves as an introduction for a series of publications that will report experimental research on various parts of the general problem of establishing these relations. Further, the correlation of existing information has made possible the formulation of satisfactory hypotheses covering the detailed mechanism of the movement (1) of liquid water in wood during the drying process and (2) of the impregnating liquid during the preservative treatment of timber.

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